Solid-State Coulometric Titrations and Electrical Conductivity Measurements of $La_{0.2}Sr_{0.8}Cr_{0.2}Fe_{0.8}O_{3-\delta}$

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Introduction

Oxides with the perovskite structure have been widely studied because they are candidate materials for applications in solid oxide fuel cells, as perm-selective membranes for oxygen separation, and in syngas production. The oxides should have both high electrical conductivity and good chemical stability for industrial uses. Many groups have studied the solid-state chemistry of perovskite structure oxides such as $La_{1-x}Sr_xCoO_{3-\delta}$ and various $(La,Sr)(Fe,Co)O_3$ compositions. These oxides show high oxygen permeability but are unstable in very reducing conditions. The stability of the cobaltite and the ferrite can be improved by doping Cr or Ti cations, and compositions such as $La_{0.2}Sr_{0.8}Cr_{0.2}Fe_{0.8}O_{3-\delta}$ are stable at oxygen pressures characteristics of syngas environments. Little information is available about the defect chemistry of the doubly doped ferrites.

We have performed solid-state coulometric titration and electrical conductivity measurements on $La_{0.2}Sr_{0.8}Cr_{0.2}Fe_{0.8}O_{3-\delta}$ in the temperature range 750°C~1060 °C and the pO_2 range, 10^{-18} ~ 0.5 atm. From the results, information on the defect structure and thermodynamics has been obtained.

Experimental

Conductivities and oxygen nonstoichiometry changes ($\Delta\delta$) as a function of the oxygen partial pressure (pO_2) were observed simultaneously by using the electrochemical cell shown in Figure 1. The $\Delta\delta$ changes in a sample were measured step by step by coulometric titration. A titration proceeded from a low pO_2 region ($\approx 10^{-15}$ atm) up to the air reference gas. A known amount of oxygen was pumped into the cell at each step. When the oxygen sensor reached a steady-state value, the pO_2 inside the cell and $\Delta\delta$ values were determined.

An ac four-point probe technique was used to monitor the conductivities. These measurements were performed at the same pO_2 intervals of the titration. The experiments were controlled by Labwindows software through a GPIB communicator.

Results

The pO_2 dependence of the electrical conductivities and oxygen non-stoichiometries are shown in Figure 2. At temperatures below 940°C, a two-phase region was observed as a plateau in the conductivity isotherm in the pO_2 region, 10^{-8}~10^{-6} atm.

As expected, the pO_2 at which the p-n transition occurs increased as the temperature increased. An activation energy of 0.76eV was estimated for the ionic conductivity from an Arrhenius plot of the minimum conductivity versus temperature.

The slope of the p-type conductivity isotherms varied depending on the value of pO_2. Values of 1/5 and 1/7~1/8 were observed in the pO_2 ranges 10^{-5} ~ 10^{-1} atm and 10^{-11}~10^{-7} atm respectively. Since the A-site of the sample was highly doped with Sr, ideal behavior is unlikely even in oxidizing conditions.

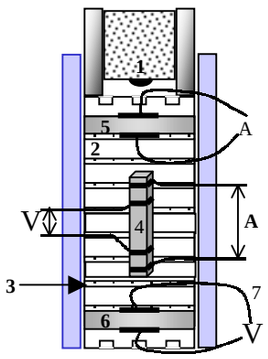

Fig. 1 Cell used for coulometric titrations and conductivity measurements 1: thermocouple, 2: alumina ring, 3: glass ring, 4: sample, 5: YSZ sensor, 6: YSZ pump, 7: Pt wire

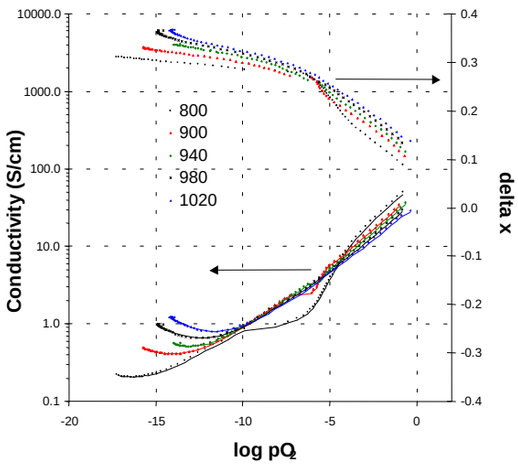

Fig. 2. pO_2 dependence of the conductivity and oxygen non-stoichiometry